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Reexamination of Method for Determination of Thermodynamic Polymer-Solvent Interaction Parameter χ of Multicomponent Polymer/Single Solvent System using Phase Separation Data

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Reliability of the method, proposed by Kamide et al. (1984), for determining temperature- and concentration-dependencies of the thermodynamic interaction parameter χ of multicomponent polymer/single solvent system by comparing experimental cloud point curve and empirical relations between temperature and relative amount of polymer partitioned in the polymer-rich phase ρ_P. with corresponding theoretical ones was examined. The method was strictly applied to atactic polystyrene/cyclohexane system by repeating the cycle of calculation procedure sufficient times until getting the self-consistent temperature- and concentration-dependent coefficients of χ. It was demonstrated for the above system that the temperature- and concentration-dependent coefficients of χ can be evaluated accurately from these phase separation data.

Key words: Cloud Point Curve, χ Parameter, Temperature Dependence Parameter, Concentration Dependence Parameter, Relative Amount of Polymer

1. Introduction

In a series of theoretical studies on the cloud point curve (CPC)[1,2], the shadow curve (SC)[1,3], the coexisting curve (CC)[2,4-8], the critical solution point (CSP)[1,9,10] and stability of CSP[3] of multicomponent polymer/single solvent system, Kamide and his coworkers proposed a method of determining the temperature- and the polymer concentration-dependencies of thermodynamic polymer-solvent interaction parameter χ by comparing both CPC data and of experimental relation between relative amount of polymer partitioned in a polymer-rich phase (PRP) ρ_p (=weight of polymer in PRP/total weight of polymer) and phase separation temperature T_P with the corresponding theoretical ones[1]. Hereafter this method is simply referred to as Kamide et al.'s CPC method. Here, χ can be written semi-empirically in the form:[1-3,9,10]

$$\chi = \chi_0\left(1+\sum_{j=1}^{n} p_j v_p\right) \tag{1}$$

where

$$\chi_0 = a + \frac{b}{T}, \tag{2}$$

$$a = 0.5 - \psi_0, \tag{3a}$$

$$b = \psi_0\theta. \tag{3b}$$

a and b are the temperature dependent parameters, p_j, the j-th concentration dependent parameter (j=1, 2, ..., n), ψ_0, the entropy parameter and θ, the Flory temperature. In eq 2, we

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Table I. Temperature-(a and b in eq 2) and concentration-(p_1 and p_2 in eq 1) dependence parameters of themodynamic interaction parameter x, Flory entropy parameter ψ_0 and Flory theta temperature θ for atactic polystyrene/cyclohexane system (T=299K).

Author(s)	Method	a	b	p_1	p_2	ψ_0	θ/K	ref.
Krigbaum and Geymer (1959)	Osmotic Pressure	0.2469	76.67	0.630_4	0.480_8	0.25	302.9	11
Scholte (1970)	Ultracentrifuge	0.2631	74.31	0.534_4	0.430_4	0.24	313.7	12
Koningsveld et al. (1970)	Critical point	0.2035	90.50	0.610_6	0.920_7	0.30	305.2	13
Koningsveld et al. (1970)	Critical point	0.2211	85.313	0.622_2	0.289_1	0.28	305.9	14
Kuwahara et al. (1973)	Threshold cloud point	0.2798	67.50	0.607_3	0.512_1	0.22	306.5	15
Kamide et al.(1984)	Cloud point curve and ρ_p vs. T relation	-0.02424	158.79	0.643	0.200	0.52	305.2	1
Kamide and Matsuda(1984)	Critical point	0.23	82.37_7	0.642	0.190	0.27	305.1	9
Kamide et al.(1995)	Cloud point curve and ρ_p vs. T relation	0.23	82.89	0.600	0.460	0.27	307.0	This work

*ρ_p, the relative amount of polymer partitioned in polymer-rich phase

*T, tempetrature

neglected the molecular weight dependence of χ_0. Two coefficients p_1 and p_2 (i.e., n=2) are enough to represent CPC data[9,10] and eq 1 can be simplified as

$$x=x_0(1+p_1v_p+p_2v_p^2). \quad (4)$$

In a previous paper,[1] this method applied to atactic polystyrene (PS)/cyclohexane (CH) system, whose thermodynamic properties were the most comprehensively studied, obtaining $a=-0.242_4$ and $b=158.79$; $p_1=0.643$ and $p_2=0.200$ as listed in Table I.

These parameters can also be evaluated by other methods including osmotic pressure,[11] ultracentrifuge[12], CSP[9,13,14] and threshold cloud point[15] methods. Table I also collects literature data on temperature- (a, b), concentration- (p_1, p_2) dependence parameters of χ, estimated by various methods and entropy parameter χ_0 and Flory temperature θ, both calculated from a, and a and b, respectively, for atactic polystyrene/cyclohexane system.[16] Note that parameters a, b, p_1 and p_2 were recalculated by Kamide et al.[1] from the original literature data available, and ψ_0 and θ were calculated in this study. The values of a and b evaluated by Kamide et al.'s experimental CPC method are significantly different from those ($a=0.24\pm0.02$ and $b=79.5\pm11$) determined by other methods; a by Kamide et al.'s CPC method is unexpectedly negative and its absolute magnitude is only 1/10 and b by Kamide et al.'s method is approximately twice of the corresponding value evaluated by other methods.

As p_1 and p_2 are concerned, however, these values estimated by Kamide et al.'s CPC method are within the scattering of those by other methods and we obtain $p_1=0.608$ and $p_2=0.47$ for this polymer/solvent system on average. This fact approved the overlooking of unusual magnitude of a and b, determined by CPC method. It should be noted that in the previous paper[1] only one cycle of calculation was carried out for estimating a, b, p_1 and p_2 by Kamide et al.'s method, mainly due to the extremely long CPU time of the computer utilized more than decade ago and that the self-consistency of a, b, p_1 and p_2 obtained were not, in strict sense, examined.

In this article an attempt was made to redetermine the parameters a, b, p_1 and p_2 of χ parameter by analyzing the same experimental data of CPC and ρ_p vs. Tp relation obtained on previous study[1], in comparison with computer simulation for atactic polystyrene/cyclohexane system, and to re-examine the reliability of Kamide et al.'s CPC method proposed previously.[1]

2. Theoretical background and method of calculation of temperature- and concentration-dependence parameter of χ parameter

General theory of phase equilibrium of polydisperse polymer/single solvent system has been established by Kamide and his coworkers[1,2,9,10] On the basis of the theory, the methods for calculating CPC[1,2] and CC[4-6] of the system have been proposed by them.

Kamide et al.'s CPC method for determination of parameters a, b, p_1 and p_2 can be briefly summarized as : These parameters can be unambiguously determined when the cloud point temperature TCP, experimentally determined (referred to as T_{CP}(exp)), coincides with that calculated by computer simulation, T_{CP}(theo), for any solution. Kamide and his coworkers proposed the following procedure to evaluate these parameters ;[1]

(1) Determine experimental CPC (i. e., the relation between T_{CP} and the polymer volume fraction v_p).

(2) Determine the relation between ρ_p (ρ_p is the weight ratio of the polymer partitioned into the polymer-rich phase to the polymer dissolved in the initial solution), and phase separation temperature T_p from the two-phase equilibrium experiments.

(3) Carry out computer simulation using arbitrarily chosen values of p_1 and p_2 (for example, $p_1 = 2/3$ and $p_2 = 2/4$ as the theoretical values for non-polar polymer/non-polar solvent systems[16]) to obtain the relation between χ_0 and ρ_p.

Kamide et al. demonstrated that CPC, unlike CC, cannot be explained by a single p_1 alone, but both p_1 and p_2 are necessary to represent the concentration dependence of χ.

(4) Construct the relation between χ_0 and 1/T using ρ_p vs. T_p relations obtained in step (2) and χ_0 vs. ρ_p relations obtained in step (3) and determine a and b as the intercept and slope of χ_0 vs. 1/T plot, respectively.

(5) Calculate CPC (T_{CP} (theo) vs. v_p relations) using a and b obtained in step (4) and using p_1 and p_2 assumed in step (3).

A theoretical method was proposed by Kamide et al. for calculating CPC of solution of polydisperse polymer in a single solution (i. e., quasi-binary system) on the basis of the polydispersity (the weight- and number-average molar volume ratio of the polymer to the solvent (degree of polymerization) of the polymer sample and temperature- and molecular weight-dependence of the polymer-solvent thermodynamic interaction parameter χ (see Figure 1 of ref, 1).

(6) Compute δ defined by

$$\delta \equiv \sum_N \{T_{cp}(\text{exp}) - T_{CP}(\text{theo})\}^2/N \quad (5)$$

(N is the total number of the solutions, for which the cloud point was determined) and determine a suitable set of p_1 and p_2 to minimize δ (where $N \geq 2$) for a given combination of a and b.

(7) Compare p_1 and p_2 thus estimated in step (6) with those assumed in step (3).

(8) If the differences p_1(step (6)) $-$ p_1(step (3)) and p_2(step (6)) $-$ p_2(step (3)) are not within the predetermined limit, repeat steps (3)$-$(7) and evaluate self-consistent parameters, a, b, p_1 and p_2.

Figure 1 shows the procedure of determining the self-consistent a, b, p_1 and p_2.

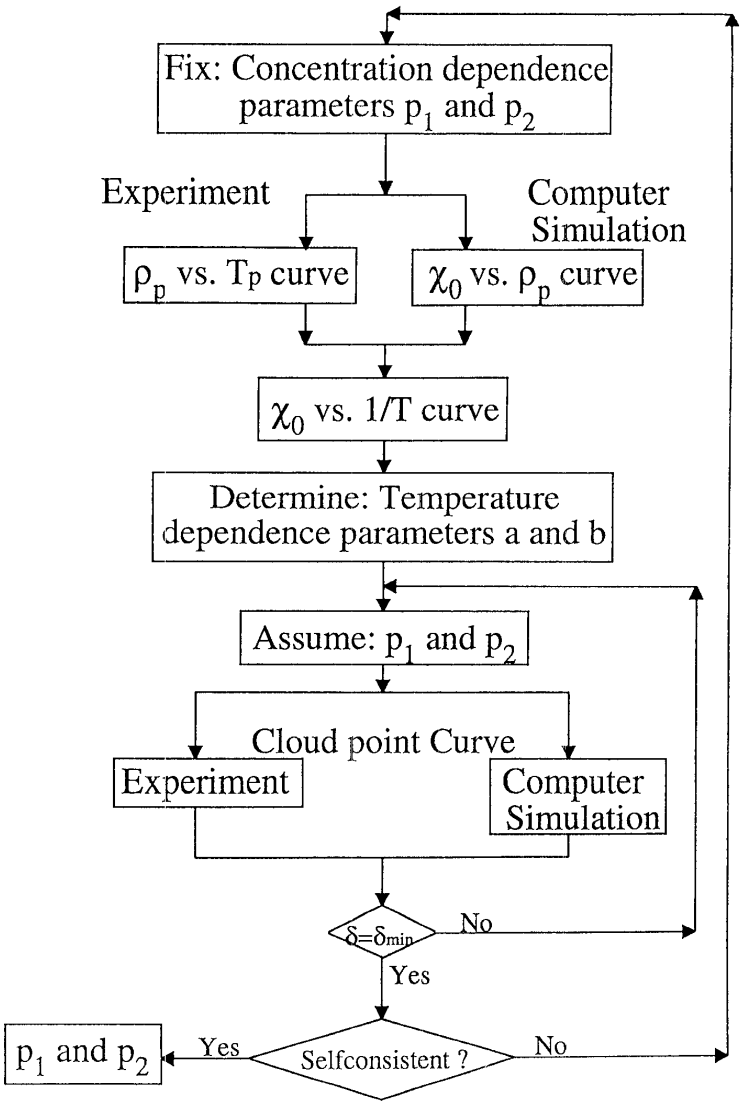

Figure 1. Scheme for determining the self consistent a, b, p_1 and p_2 by comparing the experimental cloud point and ρ_p vs. T_p curves with the corresponding theoretical curves.

3. Results and discussion

The atactic PS sample employed here is Styron 666® (Asahi Chemical Industry Co., Ltd. Tokyo) with the weight-average molecular weight $M_w = 2.43 \times 10^5$ (by the light scattering method) and the ratio of M_w to the number-average molecular weight M_n (by the membrane osmometry), $M_w/M_n = 2.8$ (i. e., the weight-average ratio of the molar volume of polymer to solvent $X_w = 2117$ in CH at 20°C). The molecular weight distribution, as evaluated by gel permeation chromatography, of the sample was reasonably expressed by a Schulz-Zimm distribution[6,18].

CPC of this PS/CH system is reproduced from ref. 1 in Figure 2 (step 1). The empirical relationships between ρ_p and T_p determined for three PS/CH solutions with initial polymer volume fractions $v_p^0 \times 10^2 = 0.45$, 0.889 and 1.306 are also reproduced from literature[1] in Figure 3 (step 2).[1]

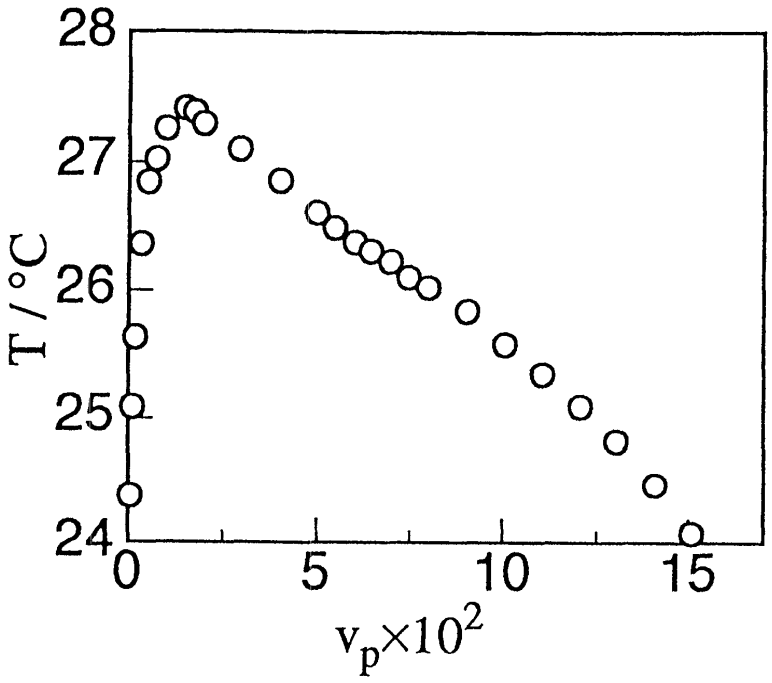

Figure 2. Experimental cloud point curve of an atactic polystyrene sample ($M_w = 2.4 \times 10^5$ and $M_w/M_n = 2.8$)/cyclohexane system.[1]

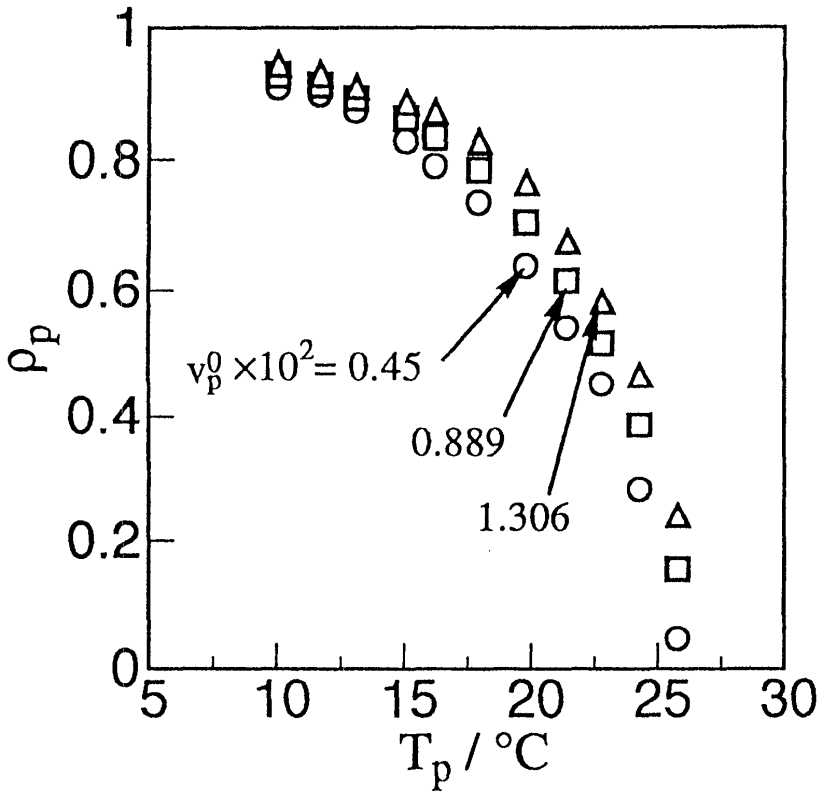

Figure 3. Experimental relations between ρ_p and T_P for an atactic polystyrene sample ($M_w = 2.4 \times 10^5$ and $M_w/M_n = 2.8$)/cyclohexane system.[1]

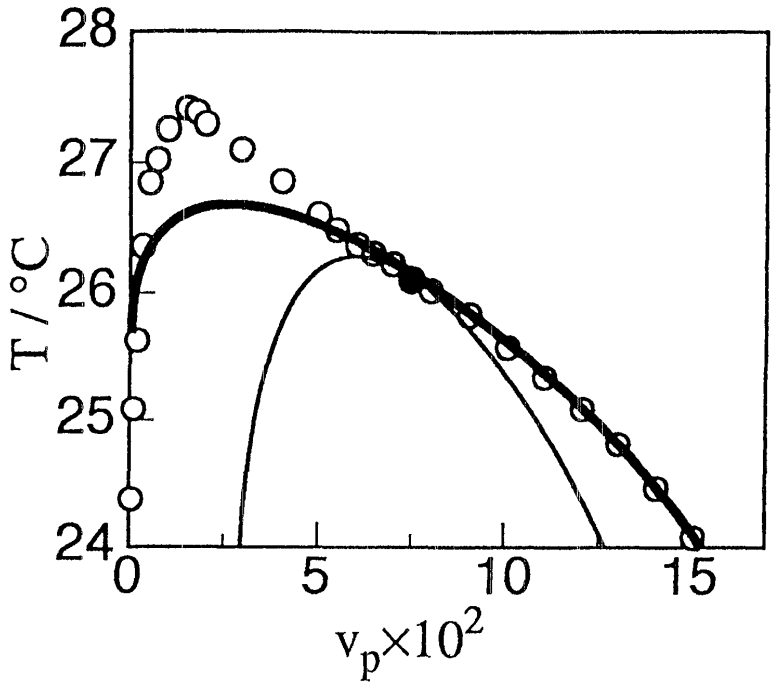

Figure 4. Cloud point curve of polystyrene ($M_w = 2.4 \times 10^5$ and $M_w/M_n = 2.8$)/cyclohexane system : ○, experimental data ;[1] broad full line, theoretical curve calculated using $p_1 = 0.600$, $p_2 = 0.460$, $\psi_0 = 0.27$ and $\theta = 307.0$K. Fine full line, theoretical spinodal curve ; ●, theoretical critical solution point. Here, a = 0.23, b = 82.89, $p_1 = 0.600$ and $p_2 = 0.460$ were utilized for calculation of spinodal curve and critical solution point.

Steps 3−5 were repeated by applied to this system. All calculations were performed using FACOM M360. Finally we obtained for atactic PS/CH system : a = 0.23, b = 82.89, $p_1 = 0.600$ and $p_2 = 0.460$. These values are con filed in the bottom line of Table Ⅰ. Reevaluated values of a and b are in fairly good agreement with average values of a (0.24) and b (79.5), respectively. Therefore, it is confirmed that significant deviation of magnitude of a and b in a previous paper[1], evaluated by Kamide et al.'s method using CPC and $\rho_p - T_p$ relation data, from those by other methods is unquestionably due to insufficient repetition of calculation cycle (step (3)−step (6)) as anticipated.

Then, χ for PS/CH system can be expressed as function of temperature (T in °K) and polymer concentration (volume fraction) as

$$\chi = \left\{0.23 + \frac{82.89}{T}\right\}(1 + 0.600 v_p + 0.460 v_p^2) \tag{6}$$

The chemical potential of the solvent in polymer solution $\Delta\mu_0$ is generally given by[16]

$$\Delta\mu_0 = \tilde{R}T\left\{\ln(1 - v_p) + \left(1 - \frac{1}{X_n}\right)v_p + \chi v_p^2\right\} \tag{7}$$

Substitution of eq (6) into eq (7) enables us to calculate $\Delta\mu_0$ over quite wide range of X_n, v_p for atactic polystyrene/cyclohexane system.

ψ_y and θ were also calculated from a and b using eq (3a) and (3b) and listed in Table Ⅰ.

Figure 4 shows the experimental CPC (open circle) and the theoretical CPC(bold line), calculated by Kamide et al.'s method using the value of a, b, p_1 and p_2 estimated in this article. In

the figure, the critical solution point (CSP) (filled circle) and spinodal curve (SC) (narrow full line) also calculated by Kamide et al.'s procedure[1,9,10] using the same a, b, p_1 and p_2 data are shown. As the theory requests, CPC and SC coincides at CSP. The theoretical CPC agrees well with the experimental CPC except the threshold point region. Although as early as 1984 Kamide et al. suggested that the above inconsistence at lower v_p region may be due to the neglect of the molecular weight dependence of χ parameter[1], any effort to dissolve this disagreement in the line of the above suggestion has ended in failure although Kamide was too optimistic in his monograph in1989,[19] so , this is even now undissolved problem.

In conclusion, (1) it is confirmed that a, b, p_1 and p_2 can be evaluated accurately by use of experimental and theoretical cloud point and ρ_p vs. T_p curves. (2) p_1 values estimated by various methods are almost coincident with each other in the region $p_1=0.60-0.64$. (3) Although p_2 values scatter in the range from 0.2 to 0.9, we can get the more reliable value (i.e., 0.460). (4) ψ_0 decreases from 0.52 to 0.27 and almost agrees with the values of other methods. (5) θ by our method is by 1.8°C higher than the previous θ (305.2°C) approaching to the value of Kuwahara et al. (306.5K). These points support strongly the idea that the modified Flory-Huggins theory, derived by introducing the concentration dependence of the χ parameter into their original theory, can be regarded as valid and accurate enough to express the thermodynamic property of actual polymer/solvent system.

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